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STATISTICAL CHARACTERIZATION OF 18650-FORMAT LITHIUM-ION CELL THERMAL RUNAWAY ENERGY DISTRIBUTIONS

BY,

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BACKGROUND: NASA AND BATTERIES

- **Lithium-ion (Li-ion) batteries are used for many aspects of human spaceflight:**
  - Solar energy storage for the International Space Station (ISS)
  - Power supply during deep space exploration with Orion
  - Power supply to astronauts during extra-vehicular activities (EVAs)
  - Robotic applications (e.g. Robonaut 2)
  - Small electronics and portable devices
- **Safety concerns exist for Li-ion battery utilization due to the inherent possibility of thermal runaway (TR)**
- **NASA's strategy for human spaceflight battery safety involves the following[1,2]:**
  - Controls to prevent overcharge/discharge, over heating, and over current
  - Manufacturer audits and extensive cell screening
  - Thermal management systems capable of preventing propagation
  - Updated the battery certification requirements to include the evaluation of TR severity and potential mitigation measures (20793 Rev D)
- **To design optimized, high performance Li-ion battery assemblies that are safe, knowledge of the following are required [3]:**
  - Total energy output range during TR for a single Li-ion cell
  - Fraction of the TR energy that is transferred through the cell casing
  - Fraction of the TR energy that is ejected through cell vent/burst paths

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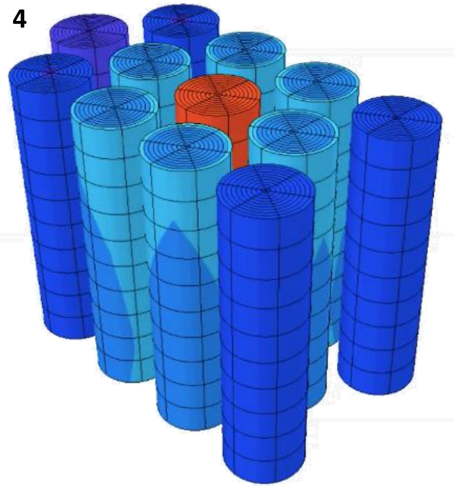

What cell should I select?

How far apart should I space my cells?

How much heat do I need to remove from the local system?

Do I need an interstitial material?

How do I best protect the adjacent cells with minimal additional mass / volume

How do I support the design with thermal analysis? What is my simulated energy distribution?

1 NASA JSC-20793 Rev D (2017).
2 Yayathi, S., et. al., Thermal Fluids and Analysis Workshop (2016).
3 Darcy, E., et. al., Advanced Automotive Battery Conference (2017).
4 Walker, W., Thermal Fluids and Analysis Workshop (2016).

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BACKGROUND: AVAILABLE CALORIMETRY METHODS

- **Accelerating rate calorimetry (ARC) [5]:**
  - Very helpful in determining the onset temperature for TR
  - Due to the slow nature of ARC testing, cell venting occurs hours before TR
  - Early venting dries out the electrolyte
  - Dried electrolyte possibly degrades the total heat output
  - No practical means to discerning TR energy fractions
- **Bomb or steel can calorimetry [6, 7]:**
  - Adequate for determining total heat output
  - No practical means to discerning TR energy fractions
- **Copper slug battery calorimetry [8]:**
  - Effective for measuring the heat output through the cell casing
  - Does not measure the heat output through the ejecta
  - Estimates rate of mass ejected during TR
  - Must combine with bomb (steel can) calorimetry to calculate heat released through ejecta and gas
  - Again, no practical means to discern TR energy fractions

Image courtesy of Yayathi, et. al. [4]

5 Yayathi, et. al., J. of Power Sources, 329 (2016) 197-206.
6 Walters, R.N. and Lyon R.E., Report DOT/FAA/TC-15/40, March 2016.
7 Jhu, C.Y., et. al., J. of Hazardous Materials, 192 (2011) 99-107.
8 Liu, X., et. al., J. of Power Sources, 280 (2015) 516-525.

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BACKGROUND: NEW CALORIMETRY METHOD

- **NASA JSC team, in collaboration with the NESC, SAIC and NREL, developed a new TR calorimetry method capable of discerning the total heat output and the fractions of heat released through the cell casing vs. ejecta material:**
  - Acknowledgement: NESC sponsored project
- **Features of the new calorimeter:**
  - Facilitates 18650-format Li-ion cells
  - Accommodates cell designs with bottom vents (BVs)
  - Uses high flux heaters to initiate TR quickly (i.e. relevant to field failure)
  - Simple operation enables multiple experiments per day
  - Compatible with high speed X-ray videography
  - Optional interface for measuring the gas exhaust heat
  - Capable of mobile transport
- **An Energy Yield Algorithm (EYA) was developed to automatically perform the following post processing tasks:**
  - Post process temperature vs. time for each calorimeter component
  - Calculate total heat output and determine the fractions of heat released through the cell casing vs. through the ejected material
- **This presentation provides a statistical characterization of the TR behavior for several high energy (270 Wh kg^{-1}) and moderate energy (200 Wh kg^{-1}) Li-ion cell designs tested in the calorimeter:**
  - Other variables considered include bottom vent (BV), cell casing thickness, and inclusion of internal short circuit (ISC) device

Image courtesy of Finegan, Donal and ESRF

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DESCRIPTION OF CELLS TESTED

- **Calorimetry experiments have been conducted at the NASA JSC Energy Systems Test Area (ESTA) and at the European Synchrotron Radiation Facility (ESRF):**
  - 38 sets of data processed for successful tests processed to date
  - 27 of the experiments were conducted using the ESRF in conjunction with the new calorimeter
- **Normalization factors (η_{Eff}) for each cell are provided in the results to allow direct comparison of total TR energy release:**
  - η_{Eff} (kJ kJ^{-1}) is the ratio of stored electrochemical energy (kJ) to the total TR energy release (kJ)
- **Note that NASA WI-033 recommends 10 tests per cell type to characterize the TR energy distribution**

Item	Unit	LG 18650-MJ1	3.35 Ah LG 18650	Samsung 18650-30Q	Molicel 18650-J
Capacity at 100% SOC	**Ah**	3.43	3.35	3.0	2.3
Nominal Voltage	**V**	3.67	3.7	3.6	3.78
Stored Electrochemical Energy	**kJ**	45.3	44.6	38.9	31.3
Cell Mass	**g**	47	47	48	47
Special Features Tested	**-**	-	BV / ISC/ TCW	-	Separator
Number of Successful Tests	**-**	9	22	3	5
Test Facility	**-**	ESTA	ESRF	ESTA	ESRF

BV: Bottom Vent Cells
NBV: Non-Bottom Vent Cells
ISC: Internal Short Circuit Device
TCW: Thin Can Wall
S1 & S2: Two proprietary separators

This design is not yet commercially available

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STATISTICAL ASSESSMENT: LG 18650-MJ1 | 3.43 Ah | 3.67 V

Item	Unit	Average	Std. Dev.	Abs. Max	Abs. Min
Total Energy	kJ	**73.8**	8.8	**82.4**	**59.4**
Normalization Factor (η_{Eff})	kJ kJ^{-1}	1.63	0.19	1.82	1.31
Distribution $E_{Cell\ Body}$	kJ	13.7	3.6	19.3	10.2
Distribution $E_{Ejecta\ and\ Gas}$ (+)	kJ	56.6	12.8	69.1	31.0
Distribution $E_{Ejecta\ and\ Gas}$ (-)	kJ	3.5	4.3	12.7	0.4
Percent $E_{Cell\ Body}$	%	**18.8**	5.5	30.6	12.7
Percent $E_{Ejecta\ and\ Gas}$ (+)	%	**76.1**	11.4	86.7	49.3
Percent $E_{Ejecta\ and\ Gas}$ (-)	%	**5.2**	6.7	20.1	0.5
Time to Trigger	s	93.5	5.7	105.9	83.9
Cell Mass (Pre-TR)	g	47.0	0.0	47.0	47.0
Cell Mass (Post-Tr)	g	10.3	2.5	15.2	7.4
Pos. Ejecta Mating Soot Mass (Post-TR)	g	4.6	2.5	8.5	0.2
Pos. Ejecta Bore Soot Mass (Post-TR)	g	15.7	3.7	21.1	8.9
Neg. Ejecta Mating Soot Mass (Post-TR)	g	0.2	0.3	0.9	0.0
Neg. Ejecta Bore Soot Mass (Post-TR)	g	0.8	1.3	3.5	0.0
Estimated Mass Ejected from System	g	15.4	4.0	24.7	11.2

Sample Size: 9

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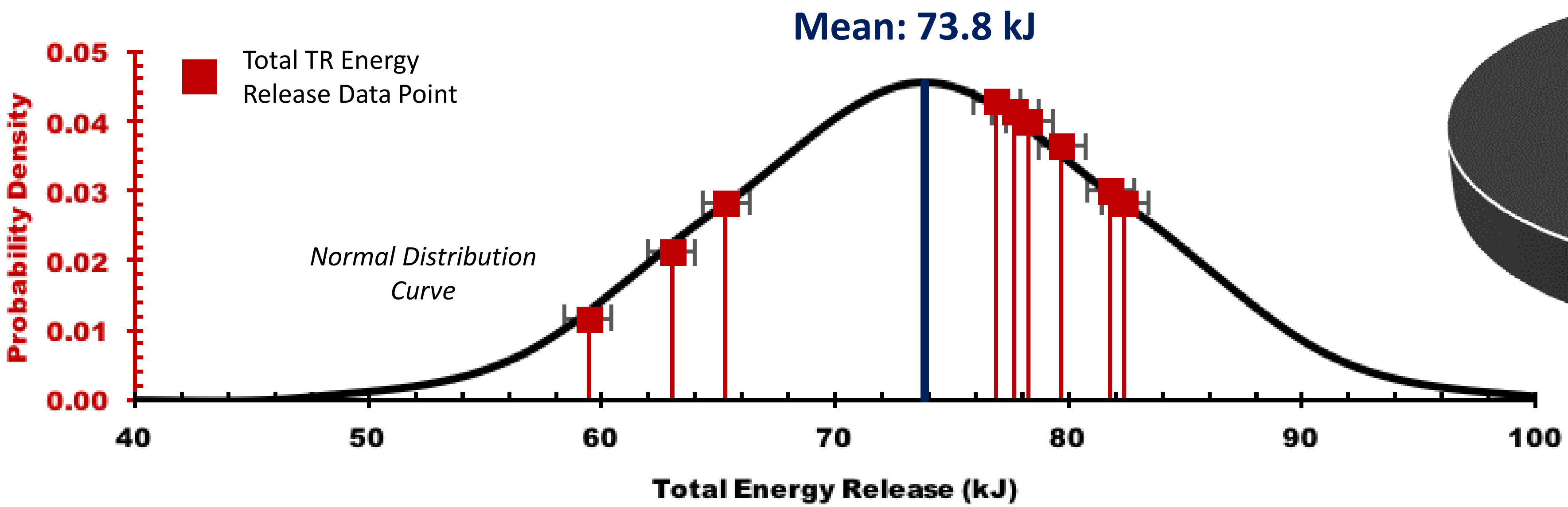
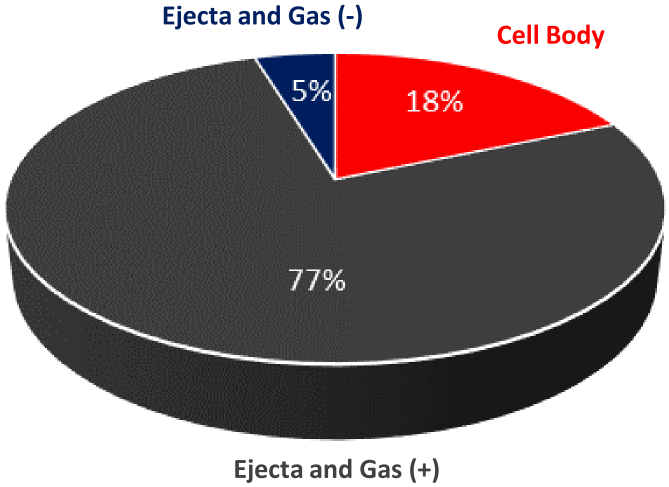
STATISTICAL ASSESSMENT: LG 18650-MJ1 | 3.43 Ah | 3.67 V

- **The LG 18650-MJ1 is the highest energy cell tested to date in the new calorimeter:**
  - Comparison to results from lower energy cells indicates that higher energy cells tend to have more violent TR events and to release a large fraction of the energy through the ejecta material and gases (on order of 80%)
  - Although more violent, less energy may be directed to the neighbor cells depending on failure mechanism
- **Large standard deviation (8.8 kJ) makes 3-sigma (3-σ) / 6-sigma (6-σ) assessment impractical**





Sample Size: 9

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STATISTICAL ASSESSMENT: 3.35 Ah LG 18650 | 3.35 Ah | 3.7 V

Item	Unit	Average	Std. Dev.	Abs. Max	Abs. Min
Total Energy	**kJ**	**63.4**	5.1	**71.7**	**55.0**
Normalization Factor (η_{Eff})	**kJ kJ^{-1}**	1.40	0.11	1.58	1.21
Distribution $E_{Cell\ Body}$	**kJ**	20.8	4.2	30.4	13.5
Distribution $E_{Ejecta\ and\ Gas}$ (+)	**kJ**	31.7	15.1	57.6	9.3
Distribution $E_{Ejecta\ and\ Gas}$ (-)	**kJ**	10.9	10.8	29.7	0.3
Percent $E_{Cell\ Body}$	**%**	**33.3**	7.9	49.4	18.8
Percent $E_{Ejecta\ and\ Gas}$ (+)	**%**	**49.1**	21.0	80.3	16.2
Percent $E_{Ejecta\ and\ Gas}$ (-)	**%**	**17.7**	17.6	51.8	0.5
Time to Trigger	**s**	58.4	22.9	**98.3**	**24.6**
Cell Mass (Pre-TR)	**g**	47.5	0.3	48.0	47.2
Cell Mass (Post-Tr)	**g**	23.0	4.0	28.5	14.9
Pos. Ejecta Mating Soot Mass (Post-TR)	**g**	0.6	0.8	3.4	0.1
Pos. Ejecta Bore Soot Mass (Post-TR)	**g**	9.9	5.1	17.8	2.9
Neg. Ejecta Mating Soot Mass (Post-TR)	**g**	0.2	0.4	1.5	0.0
Neg. Ejecta Bore Soot Mass (Post-TR)	**g**	2.3	2.8	8.8	0.0
Estimated Mass Ejected from System	**g**	11.4	2.4	19.3	8.1

Impacts of cells with BV and TCW

Sample Size: 22

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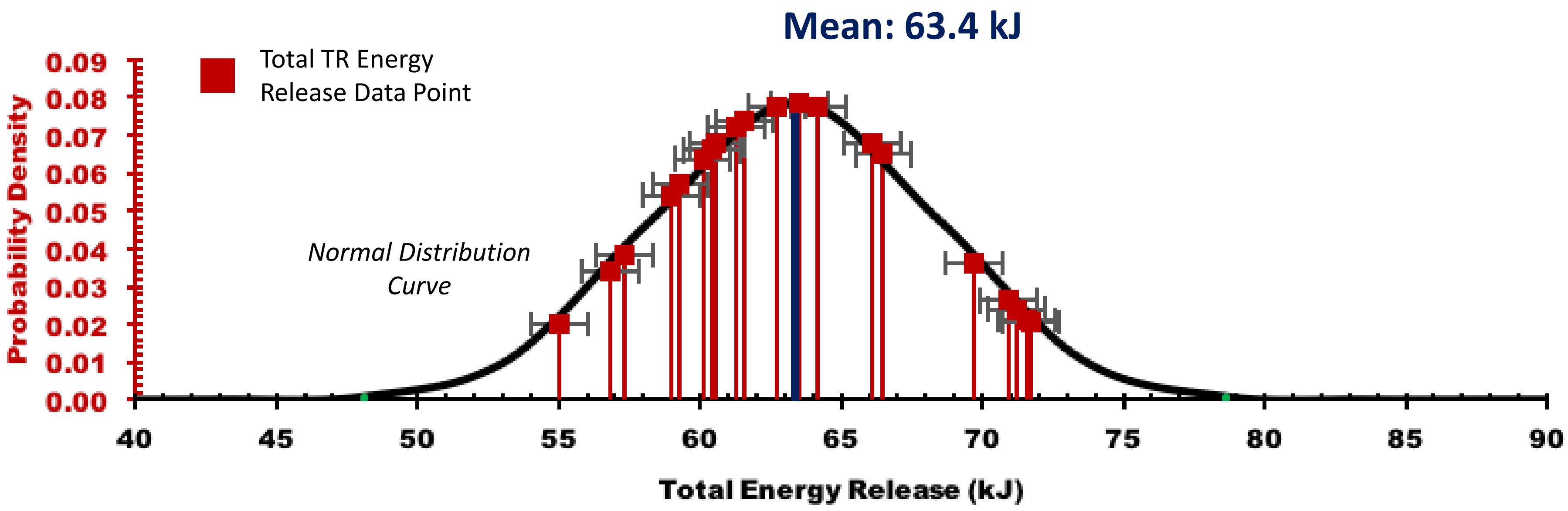
STATISTICAL ASSESSMENT: 3.35 Ah LG 18650 | 3.35 Ah | 3.7 V

- **The 3.35 Ah LG 18650 is a development cell where several features were considered:**
  - Results below combine standard cell, BV cell, ISC cells, TWC cells and combinations of each
  - Same chemistry, so direct comparison of TR energy provided below
  - Inclusion of bottom vent cells makes assessment of energy fraction not possible at this level (requires sort, see next slide…)
- **Like with the MJ1, the large standard deviation (5.1 kJ) makes 3-σ / 6-σ assessment impractical:**
  - Lower standard deviation than the MJ1 tests (5.1 kJ vs. 8.8 kJ)



Sample Size: 22

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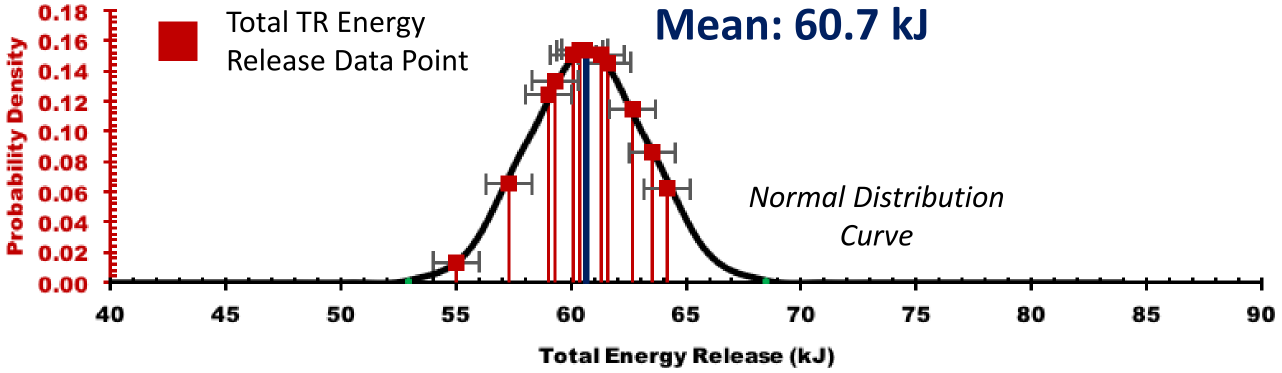
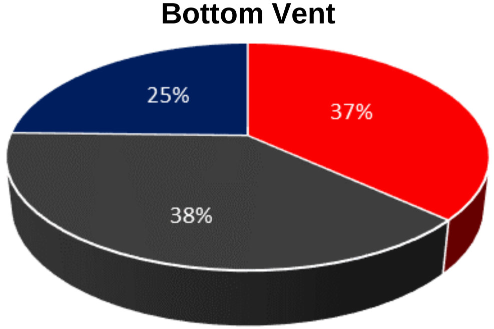
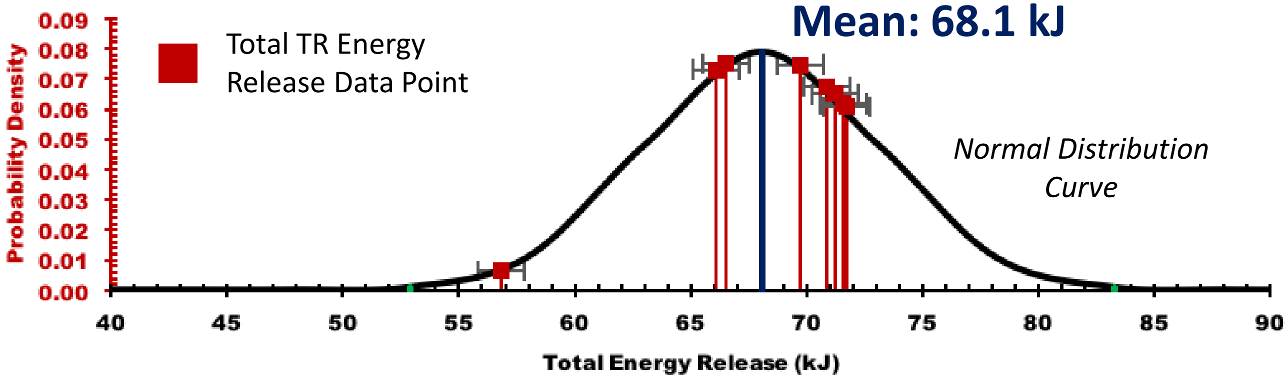
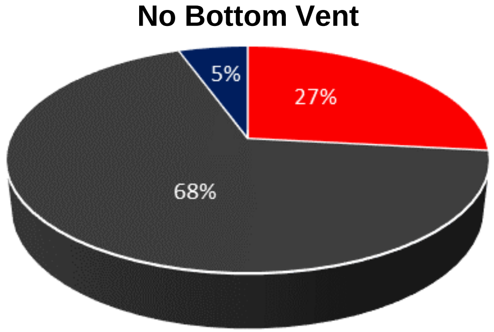
STATISTICAL ASSESSMENT: 3.35 Ah LG 18650 (BV VS. NBV)

- **BV cells had a tighter distribution (more predictable) of total TR energy release**
- **NBV cells had a higher total TR energy release, larger distribution (less predictable), and more mass loss:**
  - Possibly due to the increased "violence" associated with non-BV TR events
- **Counter-intuitively, BV cells typically had a higher remaining cell mass**
- **Standard deviation for BV and NBV makes 3-σ / 6-σ assessment impractical (2.6 kJ and 5.1 kJ, respectively)**









Cell Body
Ejecta and Gas (+)
Ejecta and Gas (-)

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STATISTICAL ASSESSMENT: 3.35 Ah LG 18650 (BV VS. NBV)

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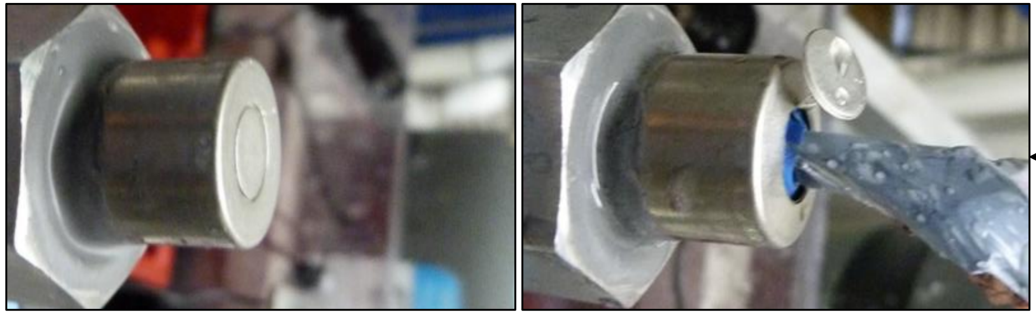
  - Possibly due to the increased "violence" associated with non-BV TR events
- **Counter-intuitively, BV cells typically had a higher remaining cell mass**
- **Standard deviation for BV and NBV makes 3-σ / 6-σ assessment impractical (2.6 kJ and 5.1 kJ, respectively)**

Total TR Energy Release Vs. Mass Loss: BV

Item	Unit	XR-Run2	XR-Run3	XR-Run4	XR-Run5	XR-Run6	XR-Run7	XR-Run8	XR-Run9	XR-Run12	XR-Run13	XR-Run16	XR-Run18	XR-Run19	XR-Run22	Average	Std. Dev.
Total Energy	kJ	64.2	63.5	60.6	64.2	59.0	60.6	60.4	59.3	62.7	57.3	55.0	60.1	61.3	61.6	60.7	2.6
Electrochemical Ratio	$kJ\ kJ^{-1}$	1.42	1.40	1.34	1.42	1.30	1.34	1.33	1.31	1.38	1.26	1.21	1.33	1.35	1.36	1.34	0.06
Cell Mass (Pre-TR)	g	47.3	47.3	47.3	47.3	47.3	47.3	47.3	47.3	47.2	47.9	47.3	47.3	47.3	47.6	47.4	0.2
Cell Mass (Post-Tr)	g	20.1	23.3	26.6	28.5	23.9	26.6	28.0	28.4	23.9	25.0	23.8	25.3	27.3	22.5	25.2	2.5

Total TR Energy Release Vs. Mass Loss: NBV

Item	Unit	XR-Run10	XR-Run11	XR-Run14	XR-Run15	XR-Run20	XR-Run21	XR-Run23	XR-Run25	Average	Std. Dev.
Total Energy	kJ	66.1	66.5	70.9	69.7	71.2	71.7	71.6	56.8	68.1	5.1
Electrochemical Ratio	$kJ\ kJ^{-1}$	1.46	1.47	1.56	1.54	1.57	1.58	1.58	1.25	1.50	0.11
Cell Mass (Pre-TR)	g	47.3	48.0	47.9	47.9	48.0	47.9	47.3	47.3	47.7	0.3
Cell Mass (Post-Tr)	g	21.1	21.2	15.8	21.5	15.7	14.9	20.8	22.7	19.2	3.2



LG cell with BV before (left) and after (right) vent/burst testing

Image courtesy of Darcy, E., et. al. [9]

9 Darcy, E., et. al., S&T Meeting, San Diego, CA. (2016).

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STATISTICAL ASSESSMENT: SAMSUNG 18650-30Q | 3.0 Ah | 3.6 V

Item	Unit	Average	Std. Dev.	Abs. Max	Abs. Min
Total Energy	kJ	**59.9**	2.5	**62.6**	**57.7**
Normalization Factor (η_{Eff})	kJ kJ^{-1}	1.54	0.06	1.61	1.48
Distribution $E_{Cell\ Body}$	kJ	11.3	5.4	17.5	7.7
Distribution $E_{Ejecta\ and\ Gas}$ (+)	kJ	48.6	6.5	54.8	41.8
Distribution $E_{Ejecta\ and\ Gas}$ (-)	kJ	0.0	0.0	0.0	0.0
Percent $E_{Cell\ Body}$	%	**18.9**	9.2	29.5	12.4
Percent $E_{Ejecta\ and\ Gas}$ (+)	%	**81.1**	9.2	87.6	70.5
Percent $E_{Ejecta\ and\ Gas}$ (-)	%	**0.0**	0.0	0.0	0.0
Time to Trigger	s	84.2	5.2	89.5	79.1
Cell Mass (Pre-TR)	g	48.0	0.0	48.0	48.0
Cell Mass (Post-Tr)	g	9.5	3.9	14.0	6.9
Pos. Ejecta Mating Soot Mass (Post-TR)	g	0.8	1.2	2.2	0.0
Pos. Ejecta Bore Soot Mass (Post-TR)	g	21.2	5.3	25.6	15.3
Neg. Ejecta Mating Soot Mass (Post-TR)	g	0.0	0.0	0.0	0.0
Neg. Ejecta Bore Soot Mass (Post-TR)	g	0.0	0.0	0.0	0.0
Estimated Mass Ejected from System	g	16.5	1.9	18.7	15.2

Sample Size: 3

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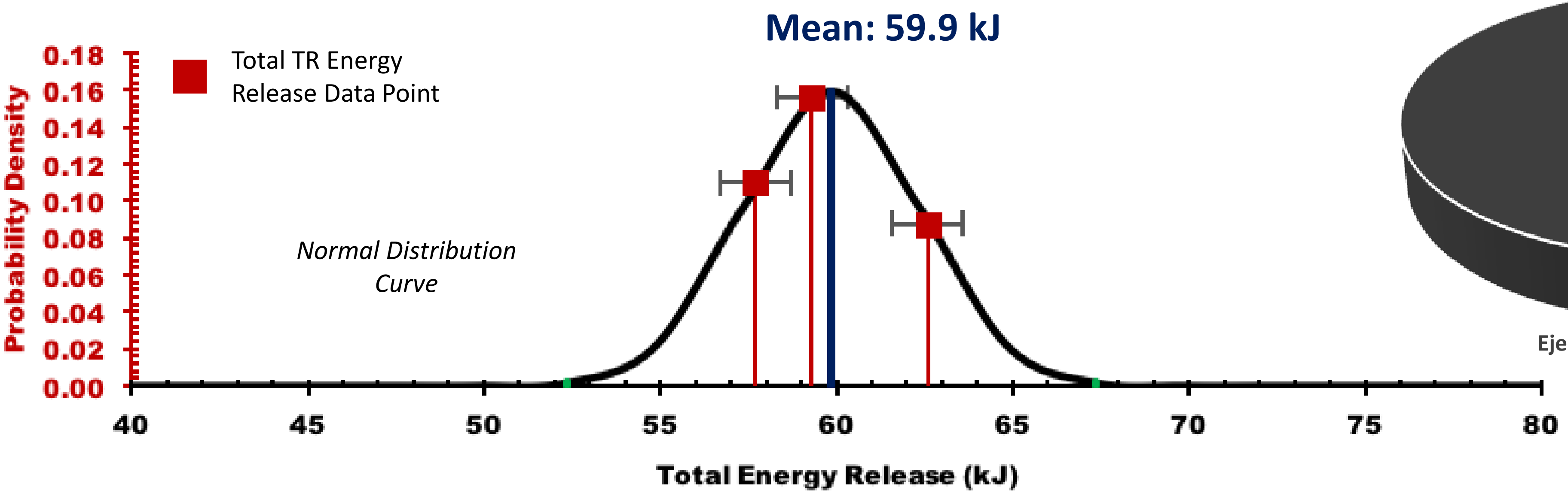
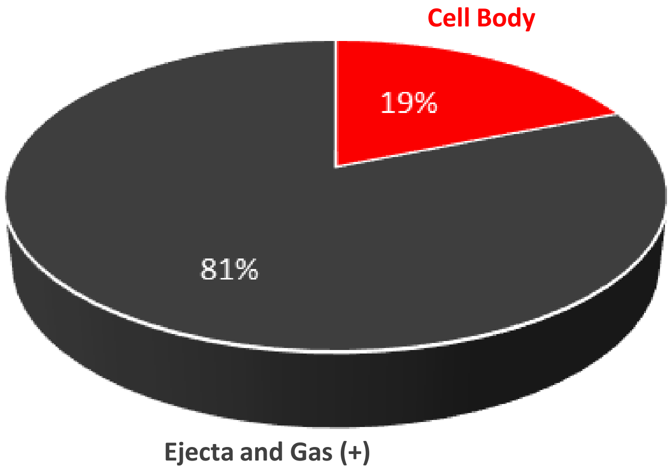
STATISTICAL ASSESSMENT: SAMSUNG 18650-30Q | 3.0 Ah | 3.6 V

- **Only 3 runs conducted so far for the Samsung 30Q:**
  - Efforts in work to conduct 7 more tests to complete the assessment of the cell
- **Again, the higher energy cells demonstrates a significant fraction of energy released through the ejecta**
- **Standard deviation (2.5 kJ) still makes 3-σ / 6-σ assessment impractical; could grow larger as more cells are tested**
- **Total TR energy release may not be directly proportional to stored electrochemical energy:**
  - Consider the Samsung 30Q energy compared to other cells when normalized to electrochemical energy
  - Samsung 30Q had a higher normalization factor (η_{Eff} of 1.54) than the 3.35 Ah LG 18650 (η_{Eff} of 1.4)





Sample Size: 3

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STATISTICAL ASSESSMENT: MOLICEL 18650-J | 2.3 Ah | 3.78 V

Item	Unit	Average	Std. Dev.	Abs. Max	Abs. Min
Total Energy	kJ	**35.5**	4.2	**41.5**	**31.1**
Normalization Factor (η_{Eff})	kJ kJ^{-1}	1.13	0.14	1.33	0.99
Distribution $E_{Cell\ Body}$	kJ	12.9	3.8	18.4	8.7
Distribution $E_{Ejecta\ and\ Gas}$ (+)	kJ	17.2	2.4	20.4	14.6
Distribution $E_{Ejecta\ and\ Gas}$ (-)	kJ	5.5	1.6	7.8	3.5
Percent $E_{Cell\ Body}$	%	**35.9**	7.5	44.2	28.0
Percent $E_{Ejecta\ and\ Gas}$ (+)	%	**48.4**	4.8	56.6	45.0
Percent $E_{Ejecta\ and\ Gas}$ (-)	%	**15.7**	5.8	25.0	10.5
Time to Trigger	s	91.9	38.5	141.9	39.6
Cell Mass (Pre-TR)	g	48.0	0.0	48.0	48.0
Cell Mass (Post-Tr)	g	34.7	0.8	36.0	33.9
Pos. Ejecta Mating Soot Mass (Post-TR)	g	0.9	1.1	2.9	0.2
Pos. Ejecta Bore Soot Mass (Post-TR)	g	2.7	1.8	4.3	0.0
Neg. Ejecta Mating Soot Mass (Post-TR)	g	0.2	0.3	0.8	0.0
Neg. Ejecta Bore Soot Mass (Post-TR)	g	0.0	0.0	0.0	0.0
Estimated Mass Ejected from System	g	9.3	0.7	10.2	8.5

Sample Size: 5

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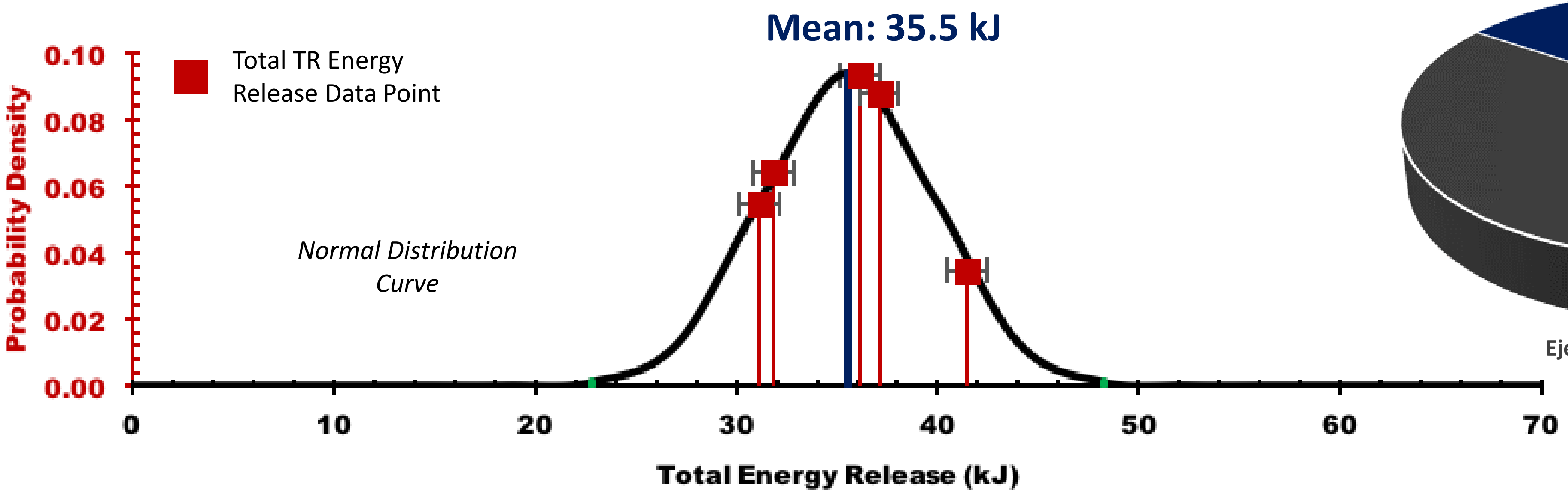
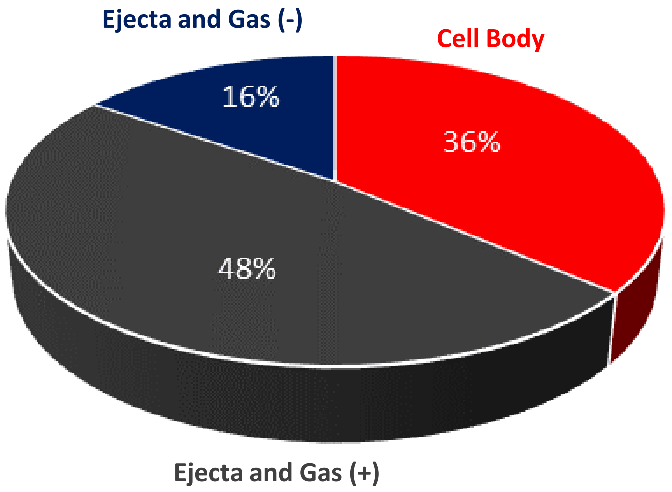
STATISTICAL ASSESSMENT: MOLICEL 18650-J | 2.3 Ah | 3.78 V

- **Only 5 runs conducted so far for the Molicel 18650-J:**
  - Two proprietary separator materials considered
- **Lower energy cell released more energy through the casing of the cell:**
  - The Molicel TR event took longer for the calorimeter to register max energy which lead to ”leach” heat to the negative side calorimeter components; this leach heat gives the appearance of bottom rupture on the pie chart
- **Magnitude of standard deviation (4.2 kJ) still makes 3-σ / 6-σ assessment impractical**





Sample Size: 5

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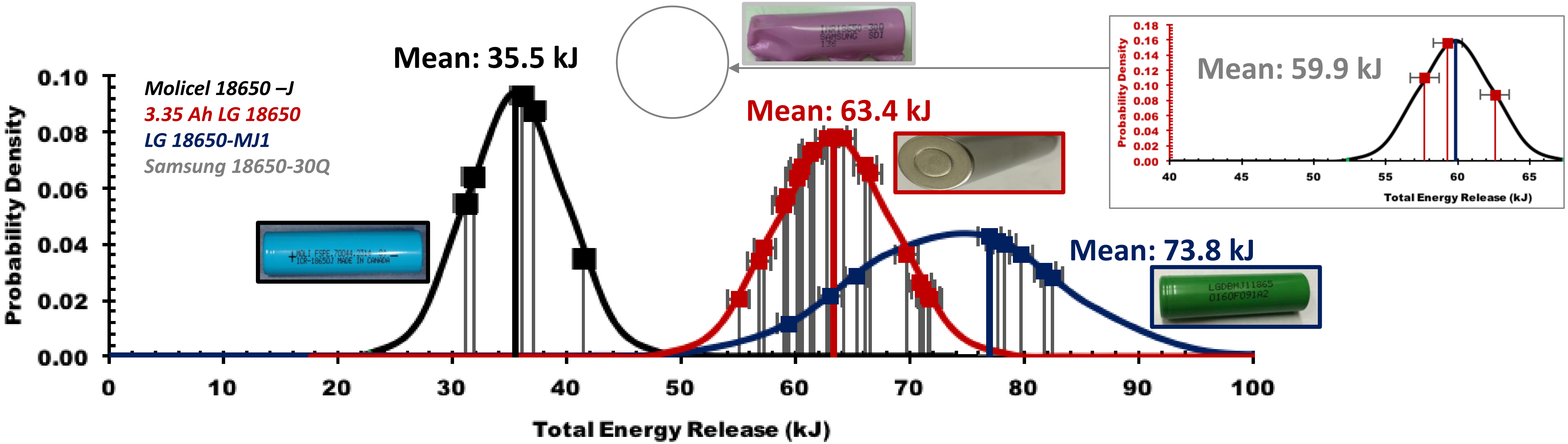
STATISTICAL ASSESSMENT: COMBINED COMPARISON

- **The predictability of TR behavior decreases as energy density increases:**
  - The 2.3 Ah Molicel 18650-J cells had the smallest standard deviation (4.2 kJ), the 3.35 Ah LG 18650 cells had slightly higher standard deviation (5.1 kJ), while the 3.43 Ah LG 18650-MJ1 had the highest standard deviation (8.8 kJ)
  - The Samsung 18650-30Q standard deviation is excluded here due to small sample size (3)
  - Indicates that higher energy cells have more severe TR events which are generally less predictable
- **However, the introduction of the BV to higher energy cells disrupts the previously described behavior (refer to Chart 10):**
  - After excluding the non-BV versions, the 3.35 Ah LG 18650 cells with BV, had the lowest standard deviation of 2.6 kJ
  - Suggests that the predictability of higher energy cells can be improved with inclusion of BV



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CONCLUSION

- **New calorimetry method that was used for the testing that these results are generated from enables the discernment of the fractions of TR energy released through the cell casing and through the ejecta material**
- **Results provide the means to develop optimized Li-ion batteries while also maintaining safety aspects and margin**
- **Thermal analysis efforts could consider the following options:**
  - First, consider the impacts of 100% worst case TR energy released through the cell casing
  - Second, consider 100% of the highest probability TR energy released through the cell casing
  - Third, consider the worst case fraction of the worst case TR energy released through the cell casing
  - Fourth, consider the average cell casing fraction of the highest probability TR energy released through the cell casing
- **Thermal analysis could also consider a 3-σ or 6-σ approach if fractions are assumed:**
  - First, consider the impacts of worst case cell casing fraction coupled with 6-σ TR energy release
  - Second, consider the impacts of worst case cell casing fraction coupled with 3-σ TR energy release
- **Although the total TR energy release is related to the stored electrochemical energy, it may not be directly proportional (e.g. comparison of the LG 18650-MJ1 to the Samsung 18650-30Q TR characteristics):**
  - Cells of varying chemistry and materials have different TR energy release probabilities (slide 20)
- **BV cells consistently released less TR energy (~10 kJ for 3.35 Ah LG cell) and have higher post TR cell mass than non-BV cells:**
  - This all indicates a less severe TR event as an effect of the BV feature
  - Battery designers should be ready to accommodate and take advantage of cell designs with the BV feature in the future
- **Higher energy cells tend to eject more material during TR:**
  - Results in less energy associated with the cell body and more energy associated with the ejecta
- **NASA WI-033 recommends 10 calorimeter experiments to characterize the TR behavior of a given cell**